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(TaC/Ta₂C) bilayer formed on carburized and annealed tantalum; development of a numerical growth model

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ABSTRACT

This paper describes a model developed to simulate the evolution of carbide layers (TaC/Ta₂C) formed during carburizing and annealing treatments of tantalum. The model is based on a parabolic evolution of the layer thickness during the growth, and on the carbon conservation during the annealing. In order to validate this model a MATLAB® program was developed. It enables the prediction of the evolution of the tantalum carbide layers (nature and thickness) for a desired treatment defined by a temperature, a carburizing and an annealing duration.

1. Introduction

Carburizing is a thermochemical treatment which increases the carbon concentration of a metallic surface in order to improve its properties such as hardness. The process used here for carburizing is described in a recent patent [1]. The carburizing gas is ethylene (C₂H₄). It is introduced continuously inside the furnace with a controlled flow while a vacuum pump maintains a vacuum level of a few millibars. The carburizing temperature is set in a domain where the diffusion coefficients and the solubility of carbon in tantalum are known [2].

The process contains two steps; firstly an enrichment with carbon and secondly a diffusion sequence. Enrichment steps have already been studied and simulated in the literature for similar systems (FeB/Fe₂B, Fe₂₋₃N/Fe₄N) [3–6] and for tantalum [7,2,8]. However, the simulation of the annealing step for a bilayer system is not developed in these studies. The purpose of the model presented in this paper is to define the duration of each step in order to obtain the desired microstructure.

The model, developed with MATLAB® software, is composed of several steps. Carburizing consists of a carbon enrichment phase (Step 1) during which two carbide layers appear: TaC on the surface and Ta₂C below. Then, annealing, which is divided into two carbon diffusion steps, leads firstly to the disappearance of the TaC layer and to the growth of the Ta₂C one (Step 2). Secondly, annealing leads to the disappearance of the Ta₂C layer (Step 3). After the treatment, the cooling

to room temperature changes the carbon solubility in tantalum, leading to a Ta₂C precipitate layer in carbon saturated tantalum.

2. Model assumptions

In this model, the following assumptions are made:

- The carbon flow on the surface is sufficient to saturate the surface and obtain TaC.
- The kinetics are driven by the growth coefficient of the layers and carbon diffusion coefficient.
- Layer evolutions are due to the carbon diffusion perpendicularly to the plane surface of the sample.
- Carbon diffusion coefficients are independent of the carbon concentration; in each layer they follow an Arrhenius law.
- The temperature is supposed to be uniform and constant throughout the sample.
- Layer thicknesses are small compared to the sample: the carbon concentration of the heart of the sample is zero.
- When the carbon source of a layer disappears, the time needed to homogenize the carbon concentration in the layer is supposed to be zero.
- The volume variation is neglected.
- Porosity, roughness and material defects are not taken into account.

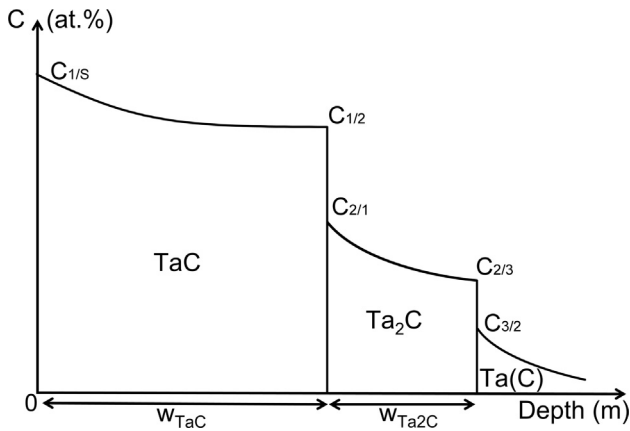


Fig. 1. Carbon profile after a carburizing process: Step 1 corresponding to carbon enrichment.

3. Layer evolution model

If the carburizing cycle of tantalum is well set, a microstructure with three different layers as presented in Fig. 1 is obtained.

For all following equations, the index i indicates to which zone the parameter refers: $i = 1$ for the TaC layer, $i = 2$ for the Ta₂C layer and $i = 3$ for the carbon solid solution in tantalum matrix.

3.1. Carbon enrichment phase (Step 1)

Enrichment phases have already been studied in the literature for similar systems like FeB and FeB₂ for boriding [3,4], Fe₂₋₃N and Fe₄N for nitriding [5,6] and also for carburizing TaC and Ta₂C [7,2,8]. During carburizing, the calculation of layer thicknesses depending on the layer growth coefficient and on the treatment duration is given by Eq. (1)

$$w_i = \sqrt{k_i \cdot t_{carb}} \quad (1)$$

With w_i the layer thickness (m), t_{carb} the carburizing duration (s) and k_i the layer growth coefficient (m²·s⁻¹). $i = (1, 2)$.

In each phase the carbon concentration is a function of the depth and responds to Eq. (2).

$$c(x_i, t_{carb}) = A_i + B_i \cdot \operatorname{erf}\left(\frac{x_i}{2\sqrt{D_i \cdot t_{carb}}}\right) \quad (2)$$

With $c(x_i, t_{carb})$ the carbon concentration (at.%) at the depth x_i (m) for the carburizing duration t_{carb} (s), D_i the carbon diffusion coefficient (m²·s⁻¹), and, A_i and B_i two constants (at.%). $i = (1, 2, 3)$.

If layer thicknesses and their limit concentrations are known (Table 1 according to Fig. 1), it is possible to calculate the carbon concentration as a function of depth. Integrating concentrations over the entire profile, the total amount of carbon diffused in the sample I_{tot} is obtained. During the following diffusion phases (annealing), this global quantity of carbon will be conserved inside the sample.

3.2. Carbon diffusion phases (Steps 2 and 3)

3.2.1. Carbon profile in the tantalum matrix

During the annealing, as long as TaC and Ta₂C layers are not

Table 1
Limit concentrations of carbon in each phase at 1600 °C according to references [9–11].

	$C_{1/5}$	$C_{1/2}$	$C_{2/1}$	$C_{2/3}$	$C_{3/2}$
Values (at.%)	50	42.5	33.3	29.0	0.40

consumed, the mobile interface Ta₂C/Ta(C) can be considered as the carbon source which enriches the tantalum matrix Ta(C). The new carbon profile in the matrix responds to an expression similar to the Eq. (2), described in Eq. (3) with a treatment duration $t_{carb} + t_{an}$:

$$c(x_3, t_{carb} + t_{an}) = A_3 + B_3 \cdot \operatorname{erf}\left(\frac{x_3}{2\sqrt{D_3 \cdot (t_{carb} + t_{an})}}\right) \quad (3)$$

I_3 is the integral of the concentration of carbon in solid solution in the tantalum matrix. Its calculation leads to two possible cases.

- If $I_3 < I_{tot}$, at least one carbide layer remains and its thickness can be calculated with the model.
- If not, the two carbide layers are consumed.

3.2.2. Carbon profile in carbide layers if $I_3 < I_{tot}$

The model assumes that as soon as enrichment stops, the carbon concentration in the TaC layer instantaneously homogenizes to its minimum value $C_{1/2}$. The same is also assumed for the Ta₂C layer: the carbon concentration takes the value $C_{2/3}$ after the disappearance of the upper layer. Carbon profiles in Fig. 2 step 2 and step 3 illustrate these hypotheses.

Cotton [12] showed that as long as the TaC layer is not totally consumed, the depth $w'_{TaC+Ta2C}$ of the interface Ta₂C/Ta(C) follows the same law as during carburizing. This leads to Eq. (4).

$$w'_{TaC+Ta2C} = w'_{TaC} + w'_{Ta2C} = \sqrt{t_{carb} + t_{an}} \times (\sqrt{k_{TaC}} + \sqrt{k_{Ta2C}}) \quad (4)$$

For a given treatment duration, the program precisely determines the position of Ta₂C/Ta(C) interface according to Fig. 2 step 2 and to the Eq. (4). The thickness of the TaC layer is initialized to that obtain after carburizing.

Then the program iteratively decreases the depth of TaC/Ta₂C interface until the integral of carbon concentrations in the new profile is equal to the integral I_{tot} after carburizing. At each iteration A_2 and B_2 constants of the Eq. (2) for $i = 2$ and $t = t_{carb} + t_{an}$ are recalculated in order to adjust the carbon profile. If the integrals are not balanced before the TaC layer totally disappears, the profile changes to the configuration of Fig. 2 step 3. The program therefore gradually reduces the thickness of Ta₂C in turn until balancing integrals.

4. Results and discussion

In the literature, the values of carbon diffusion coefficient in tantalum differ slightly from one to another [12–16]: this is probably due to the dependence of the coefficient with the material microstructure (grain size, hardening...) which is not described in these publications. The carbon diffusion coefficient in tantalum calculated by Cotton [12] by inverse analysis of the depth of Ta₂C precipitates after cooling; its value at 1600 °C is $D_c^{Ta} = 6.02 \cdot 10^{-12}$ m²/s. However, at the same temperature, the coefficient calculated by Son et al. [13] is four times greater ($23.37 \cdot 10^{-12}$ m²/s). For example, for an enrichment of 600 s, 228 min of annealing are necessary for the disappearance of TaC and Ta₂C layers with Cotton's diffusion coefficient while only 80 min are necessary with Son's coefficient. This highlights the importance of choosing appropriate data. For the present work, the values of Cotton [12] are chosen because they were calculated with the same carburizing process as that used for experiment. Moreover, the model uses a minimum carbon concentration threshold to calculate the profile of carbon in solid solution in tantalum. The value of this threshold is 0.0075 at.% because the sensitivity study shows that considering lower thresholds changes annealing time for layers disappearance by less than one percent.

In order to execute the model, the chosen values set for the Arrhenius laws leading to carbon diffusion and layer growth coefficients are referenced in Table 2. By integrating these values into the model and by setting a carburizing time, the program can return the evolution of the layer thicknesses and the surface phase during an

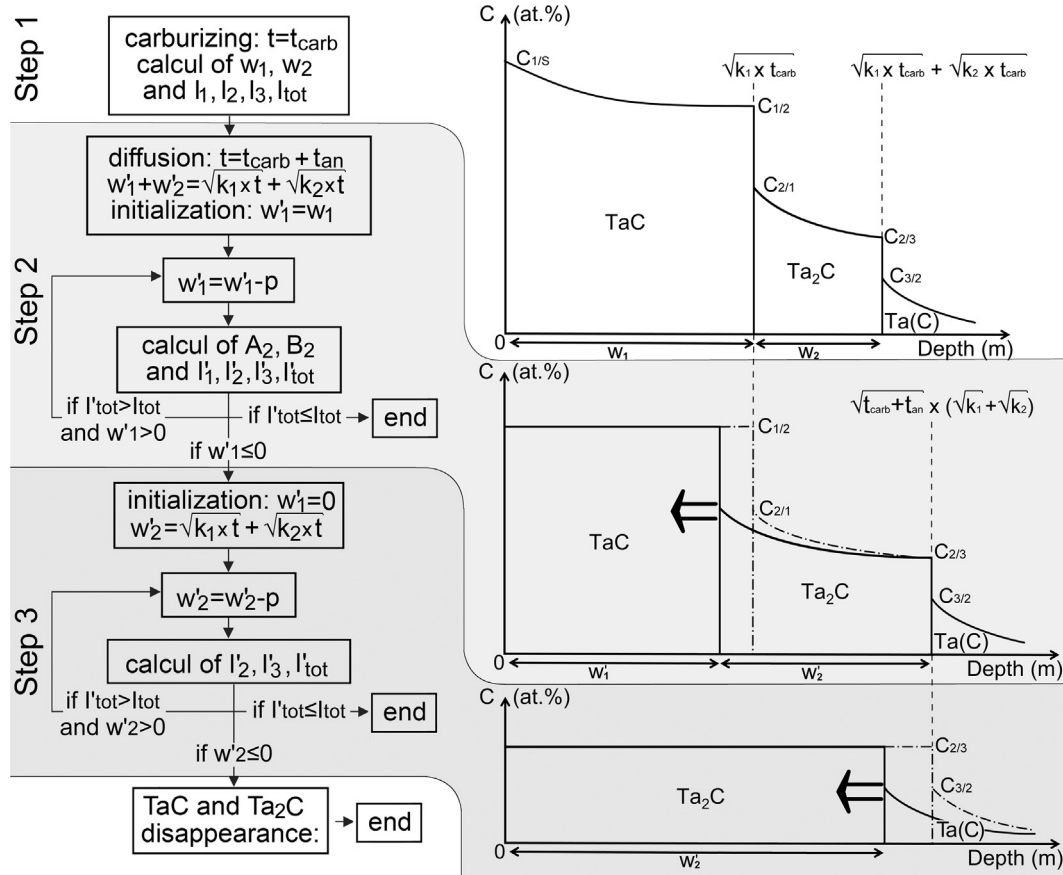


Fig. 2. Schematization of the model algorithm.

Table 2

Carbon diffusion coefficient and layer growth coefficients for each phase from 1400 °C to 2000 °C.

		Ta (C)	Ta ₂ C	TaC
Carbon diffusion coefficients	$D_0 (m^2 \cdot s^{-1})$	$1.94 \cdot 10^{-6}$ [12]	$1.27 \cdot 10^{-6}$ [7]	$1.94 \cdot 10^{-6}$ [7]
	$E (J \cdot mol^{-1})$	$197.5 \cdot 10^3$ [12]	$298.1 \cdot 10^3$ [7]	$324.9 \cdot 10^3$ [7]
Layer growth coefficients	$k_0 (\mu m^2 \cdot h^{-1})$	–	$63.25 \cdot 10^3$ [12]	$201.6 \cdot 10^3$ [12]
	$E (J \cdot mol^{-1})$	–	$168.1 \cdot 10^3$ [12]	$141.2 \cdot 10^3$ [12]

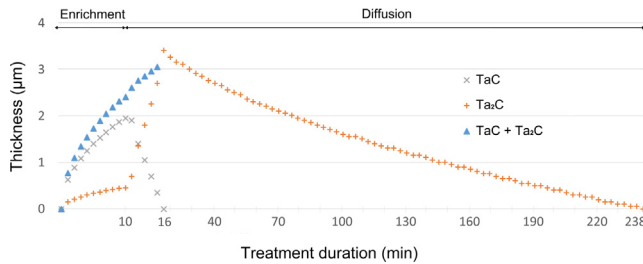


Fig. 3. Evolution of layer thicknesses during a carbon enrichment of 10 min followed by annealing at 1600 °C.

annealing. For example, for 10 min carburizing duration Fig. 3 shows the microstructure as a function of the depth and of the annealing time. This makes it possible to choose the time of treatment in order to have a desired surface microstructure.

Fig. 3 shows that after 10 min of enrichment at 1600 °C a bilayer is obtained: 2 μm of TaC on the surface and 0.5 μm of Ta₂C below. After 6 min of annealing, the surface TaC layer completely disappears in

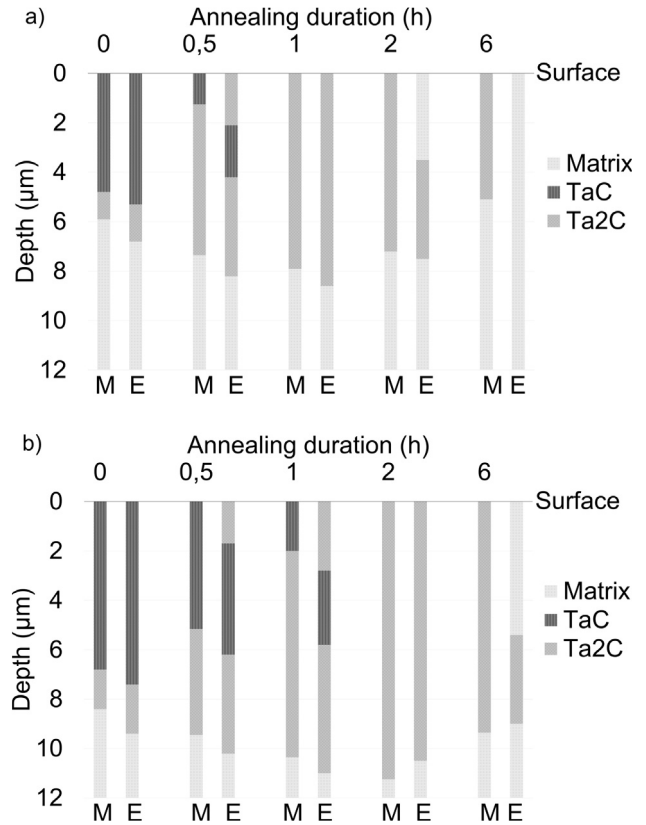


Fig. 4. Confrontation of the model (M) with the experiment (E): for carburizing of 1 h (a) and 2 h (b).

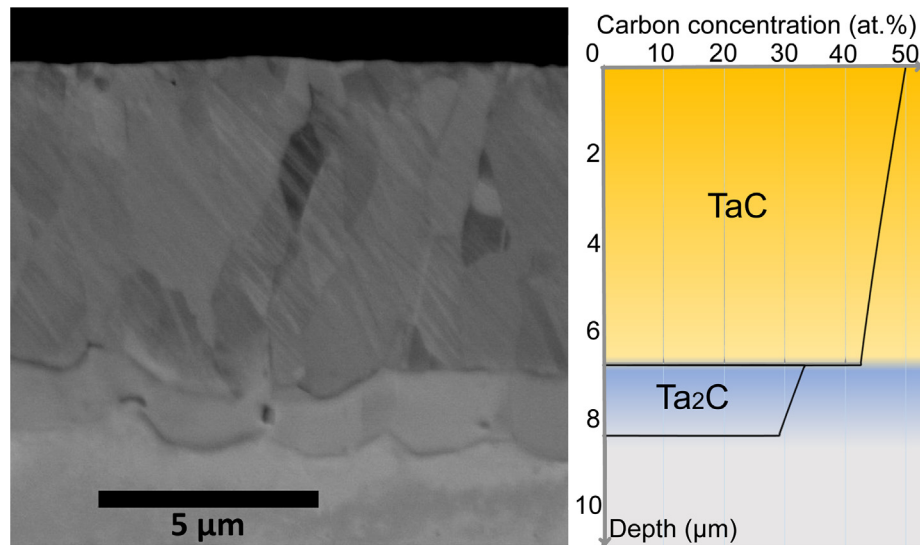


Fig. 5. Tantalum carburized 2 h at 1600 °C, SEM image (left); model prediction (right).

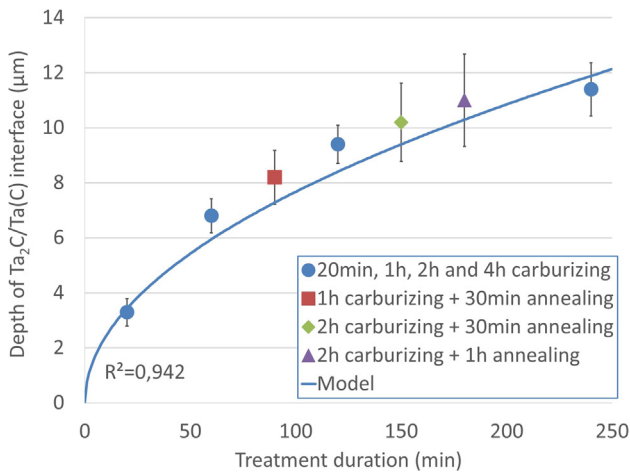


Fig. 6. Depth of Ta₂C/Ta(C) interface for carburized and annealed samples containing a TaC layer.

favour of a 3.4 μm Ta₂C layer. After 222 min of additional annealing the Ta₂C totally disappears leading to a tantalum matrix with carbon in solid solution. When cooling this microstructure, the solubility of carbon inside tantalum grains decreases and Ta₂C precipitates appear inside the tantalum matrix.

However, in Fig. 3 during the diffusion step, at the moment of the total disappearance of the TaC layer, a discontinuity is observed for the thickness of Ta₂C layer. This discontinuity is due to the hypothesis which states that the homogenization of the carbon concentration is instantaneous in the Ta₂C layer when the upper layer totally disappears.

In Fig. 4 and Fig. 5, the model is compared to experimental results obtained by Cotton [12] after 1 h of carburizing (Fig. 4a), and 2 h of carburizing (Fig. 5 and Fig. 4b). The total thickness of layers predicted with the model is in good agreement with the tests of Cotton [12]. However, for the experiment, the presence of undesired decarburization on the surface was observed during annealing. This can be correlated with the layers disappearance faster than according to the model. In Fig. 6, the depth of the Ta₂C/Ta(C) interface is plot versus the treatment duration for samples which contain a TaC layer (only carburizing or carburizing and annealing). Despite the surface decarburization, Fig. 6 shows that the TaC permits the enrichment of the underlying layer, and the position of the Ta₂C/Ta(C) interface follow the law described with

Eq. (4). Finally, in spite of the decarburization, there is a good correlation between the theoretical model and the experience.

5. Conclusion

- The evolution of TaC and Ta₂C layers during carburizing and annealing is simulated with a model which firstly considers the layers growth coefficients and then the constant quantity of absorbed carbon in tantalum during the annealing.
- This model permits to adjust treatment duration in order to obtain a specific microstructure on the surface.
- The model gives thicknesses of carbide layers in good agreements with experimental results.
- The carbon diffusion coefficient in tantalum (depending on grain size, microstructure...) is a key parameter of the model. This parameter significantly differs in the literature. For this reason, the carbon diffusion coefficient has to be estimated prior carburizing and annealing treatment to take into account the state of the raw material.
- This model can be used for similar diffusion models with bilayers like steel boriding or nitriding.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apsusc.2018.10.142>.

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